Available online at www.sciencedirect.com
ScienceDirect
Separation and Purification Technology 57 (2007) 440–443
Separation Purification Technology
www.elsevier.com/locate/seppur

Ion beam irradiation of conjugated polymers for preparing new membrane materials—A theoretical study

Zoltan A. Fekete [a,*], Eugene Wilusz [b], Frank E. Karasz [c], Csaba Visy [a]

[a] *Department of Physical Chemistry, University of Szeged, P.O. Box 105 Szeged, H-6701, Hungary*
[b] *US Army Natick Soldier Center, Natick, MA 01760, USA*
[c] *Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA*

Abstract

Conjugated polymers are attractive novel materials whose properties may be tunable after their primary synthesis, by changing their redox state along with their charge while concomitantly dedoping/redoping with appropriate counterions. They can also be made into conductive "synthetic metals" that can be incorporated into electronic circuitry in place of traditional conductors and semiconductors, besides serving as active sensing elements. Their use in sensors is already a maturing field of research, while the perspective of using them in gas separation and pervaporation applications is beginning to emerge. Permeation properties of membranes can be controlled by medium energy (up to a few hundred keV) ion beam irradiation. We present a systematic mathematical modeling approach to describing medium energy (up to a few hundred keV) ion beam irradiation, which allows to predict implantation and damage depths in any given polymer, for any ions with arbitrarily chosen atomic number and energy.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Monte Carlo simulation; Computer modeling; Ion beam irradiation; Conducting polymers; Polythiophenes; SRIM/TRIM program

1. Introduction

Ion beam irradiation is a well established tool for the modification of polymer surfaces [1–24], useful for controlled change of a variety of properties, such as chemical reactivity, hardness, wear, wetting, adhesion, and cell attachment. So far, little attention was paid to the application of this technique for modifying conjugated conducting polymers [25–30], even though in the future they may become the materials of choice [31–35] in the semiconductor industry where ion implantation is widely used. Also, besides their valuable electronic properties, these polymers have remarkable permeability characteristics as well, making them attractive membrane materials for separation [36,37] and sensor [38] applications. In this respect, it is important to note that permselectivity can be tailored by ion beam treatment [22–24,39–47].

During ion implantation, a beam of positive ions, typically with energies between 20 and 200 keV, is used to uniformly bombard the target polymer. This causes the projectile ions to be trapped in the substrate and the target to undergo structural changes due to the large amount of energy taken up from the penetrating ions [48]. The use of Monte Carlo simulation to model the effect of ion implantation into various polymers (such as polyethylene, polypropylene, polytetrafluoroethylene and polyamide) has been demonstrated in the literature [4,49,50]. The main purpose of these calculations was to estimate the penetration depths. The results from applying the TRIM code [51–53] showed near-quantitative agreement with implant profiles measured by the Rutherford back-scattering technique [4,49,50,54].

In this contribution, we extend our prior theoretical method with a more general formalism, and present the first theoretical results on ion beam implantations of poly(3-alkylthiophenes) (P3AT). These are among the most studied conjugated polymers, due to their importance in making stable conducting plastic materials. While no experimental data is available for the effect on these particular materials yet, our work on Nafion [21,22,56] already showed how promising this technique is for tailoring permeation properties; therefore these calculations can provide some guidance toward getting practical results from modifying P3AT with this relatively new technological tool. We have previously demonstrated the utility of applying the comprehensive quantum mechanical based treatment of ion–atom collisions implemented in the Stopping/Transport and Range of

[redacted]

1383-5866/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.seppur.2006.04.014

Ions in Matter program (SRIM/TRIM) [51–53,55] in modeling the effect of ion beam irradiation on some polymer membranes [21,22,56].

Our calculations have been extended by statistical analysis of the damage distribution, thus allowing an assessment of the dependence of surface layer changes on the implantation parameters. As models for P3AT with short and long sidechains, poly(3-methylthiophene) (P3MT) and poly(3-octylthiophene) (P3OT), respectively, have been chosen. After presenting our calculation method and results, an illustrative example of their use for evaluating prospective experiments is shown as well.

2. Target materials

2.1. Poly(3-methylthiophene)

Undoped P3MT, i.e. $[-(C_4HS(CH_3))-]_x$ as an infinite chain (without any end-groups) is considered, with an overall empirical formula C_5H_4S. Its density, an important input parameter to the TRIM calculations, is taken from reported helium pycnometry measurements [57] to be 1.51 g/cm^3. This corresponds to a target numerical density $N_d = 9.457 \times 10^{28}$ atoms/m^3. In evaluating our calculations, the target is characterized by an effective atomic number and atomic mass, which are simply taken as the arithmetic average values for the polymer: $Z_{eff} = 5.000$, $M_{eff} = 9.615$.

2.2. Poly(3-octylthiophene)

Undoped P3OT, i.e. $[-(C_4HS(C_8H_{17}))-]_x$ as an infinite chain (without any end-groups) is considered, with an overall empirical formula $C_{12}H_{18}S$. Its density, an important input parameter to the TRIM calculations, is taken from reported helium picnometry measurements [57] to be 1.05 g/cm^3. This corresponds to a target numerical density $N_d = 1.008 \times 10^{29}$ atoms/m^3. In evaluating our calculations, the target is characterized by an effective atomic number and atomic mass, which are simply taken as the arithmetic average values for the polymer: $Z_{eff} = 3.420$, $M_{eff} = 6.270$.

3. Calculation

Some details of our methodology have been reported earlier [22]. Briefly, penetration of projectile ions as well as the full recoil cascades are calculated by the TRIM module of the SRIM program package [51,52,55] (Version 2003.26). At each combination of projectile ion and energy investigated, statistical analysis is carried out from the raw results on both the implant ion and so-called vacancy (i.e. collisional damage) positions, to determine the moments of depth distributions [51,52,58]. The first moment is conventionally called (longitudinal) range (R_p) for the implanted ions, and we have analogously defined the range for collisional damage (R_d) [22]. The second moments are called straggling parameters; in the figures below these variance type quantities are shown plotted in place of error bars (which would be smaller than the symbols used, due to the ranges calculated with sufficient accuracy).

Job control, which involves queuing multiple SRIM/TRIM runs over sets of input data prepared, as well as evaluating and summarizing raw output, is handled by in-house developed scripts that we release to the public domain [55].

The projectile ions, chosen for this study, are the noble gases He through Rn. This covers the atomic number range 2–86, and a fit over our results allows predicting range data for arbitrary ions from the entire periodic table.

In order to summarize all the results from the different ions, converting to dimensionless units based on the Ziegler–Biersack–Littmark formalism [51,52] is performed. This utilizes scaling with the characteristic energy E_c and length R_c, defined according to Eqs. (1)–(3):

$$a_s = \frac{0.8853 a_B}{Z_1^{0.23} + Z_2^{0.23}} \tag{1}$$

$$E_c = \frac{Z_1 Z_2 e^2 (M_1 + M_2)}{M_2 4\pi\varepsilon_0 a_s} \tag{2}$$

$$R_c = \frac{(M_1 + M_2)^2}{M_1 M_2 N_d 4\pi a_s^2} \tag{3}$$

where a_s is the Ziegler–Biersack–Littmark screening length, $a_B = 0.529$ Å the Bohr radius, Z_1 and Z_2 the atomic numbers of the incident ion and target atom, respectively, M_1 and M_2 their atomic masses, $e = 1.60 \times 10^{-19}$ C the electron's charge, $\varepsilon_0 = 8.85 \times 10^{-12}$ C^2/Nm^2 the permittivity of vacuum, and N_d is the number density of the target. In order to illustrate the magnitude of these scaled quantities for selected ions, some practically relevant examples are shown in Fig. 1 (along with the resulting fits to be discussed below) for P3MT target: $E = 7$ keV helium ions, $E_c = 1.1$ keV, $R_c = 13$ nm; $E = 90$ keV sulfur ions, $E_c = 36$ keV, $R_c = 24$ nm; $E = 200$ keV xenon ions, $E_c = 483$ keV, $R_c = 95$ nm.

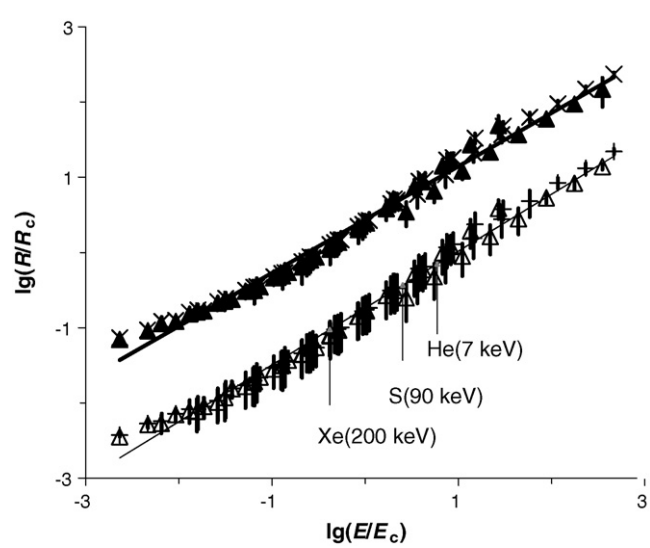

Fig. 1. Scaled ranges for implantation in P3OT (slanted crosses) and P3MT (full triangles), and for collisional damage (displaced by 1 log unit down for clarity) in P3OT (straight crosses) and P3MT (empty triangles); error bar symbols mark corresponding straggling parameters; labels designate examples of calculated collisional damage ranges into P3MT (see text for details).

4. Results and discussion

Fig. 1 displays the logarithms of scaled ranges for implant ions ($\log(R_p/R_c)$) and for collisional damage ($\log(R_d/R_c)$), versus the logarithm of scaled energy ($\log(E/E_c)$). It can be seen that all results fall on a linear master curve, when expressed in this scaled form. The corresponding straggling parameters are also shown on this plot marked by error bar symbols.

Double logarithmic fits of the scaled ranges, Eqs. (4) and (5) below (where the standard errors of the fitted slope and intercept are also shown in parentheses), show good linearity as indicated by their regression coefficient r near unity:

$$\log\left(\frac{R_p}{R_c}\right) = (0.708 \pm 0.009)\log\left(\frac{E}{E_c}\right) + (0.437 \pm 0.011), \quad r = 0.993 \tag{4}$$

$$\log\left(\frac{R_d}{R_c}\right) = (0.756 \pm 0.008)\log\left(\frac{E}{E_c}\right) + (0.262 \pm 0.011), \quad r = 0.994 \tag{5}$$

These equations allow calculating what R_p and R_d values would be yielded by a SRIM/TRIM calculation on P3AT, provided that the dimensionless energy falls in the covered range 0.002–465. Ranges for projectile ions with arbitrary Z_1, M_1 can be calculated, aiding a rational design of ion irradiation experiments.

As an example for practical utilization of the results above, let us consider the following scenario. Suppose that we want to characterize quantitatively some implantation experiments with the ECR ion source described by Dworecki et al. [24]. The projectiles in this case are 90 keV sulfur ions [24], with $\log(E/E_c) = 0.40$. Our prediction from Eq. (5) (as indicated by the corresponding label on Fig. 1) yields $\log(R_d/R_c) = 0.57$, i.e. an unscaled value of $R_d = 89$ nm. Now, in order to obtain the value of the energy necessary for getting the same damage depth with a different ion source, we can simply plug in the appropriate data for other projectiles: thus, a simple calculation gives $E = 7$ keV for He and $E = 200$ keV for Xe. These numbers can guide the setup of comparative experiments for investigating the effect of implantation treatment on the permeability of membranes.

Obviously, these calculations are only a first step toward achieving direct practical answers to separation problems. Nevertheless, given that permeation behavior is critically affected by the gas–solid interface [59–61], having the detailed quantitative description of a technique used for tailoring this region provides a helpful theoretical tool for engineering this layer.

Acknowledgements

The authors of this paper thank Dr. Thomas J. Tate for assistance with setting up the TRIM simulations, and acknowledge funding by Army Research Grant DAAD 16-01-P-0389. F.E.K. is also partially supported by the Air Force Office of Scientific Research, and Z.A.F. by the Hungarian Scientific Research Fund (OTKA grant nos. T 032190 and T 042539).

References

[1] D.V. Sviridov, Chemical aspects of implantation of high-energy ions into polymeric materials, Usp. Khim. 71 (2002) 363.
[2] L.S. Korugic-Karasz, E.A. Hoffmann, Polymer ion implantation: present and future prospects, Nonlinear Opt. Quant. Opt. 32 (2004) 135.
[3] V. Svorcik, V. Rybka, O. Jankovskij, V. Hnatowicz, Free volume-limited diffusion in ion-modified polymers, J. Appl. Polym. Sci. 61 (1996) 1097.
[4] V. Svorcik, V. Rybka, I. Micek, V. Popok, O. Jankovskij, V. Hnatowicz, J. Kvitek, Structure and properties of polymers modified by ion-implantation, Eur. Polym. J. 30 (1994) 1411.
[5] U. Myler, X.L. Xu, M.R. Coleman, P.J. Simpson, Ion implant-induced change in polyimide films monitored by variable energy positron annihilation spectroscopy, J. Polym. Sci., Part B: Polym. Phys. 36 (1998) 2413.
[6] J. Won, M.H. Kim, Y.S. Kang, H.C. Park, U.Y. Kim, S.C. Choi, S.K. Koh, Surface modification of polyimide and polysulfone membranes by ion beam for gas separation, J. Appl. Polym. Sci. 75 (2000) 1554.
[7] C. Satriano, E. Conte, G. Marletta, Surface chemical structure and cell adhesion onto ion beam modified polysiloxane, Langmuir 17 (2001) 2243.
[8] T. Ujvari, A. Toth, I. Bertoti, P.M. Nagy, A. Juhasz, Surface treatment of polyethylene by fast atom beams, Solid State Ionics 141 (2001) 225.
[9] C. Satriano, S. Carnazza, S. Guglielmino, G. Marletta, Differential cultured fibroblast behavior on plasma and ion-beam-modified polysiloxane surfaces, Langmuir 18 (2002) 9469.
[10] C. Brun, M. Fromm, F. Berger, P. Delobelle, J. Takadoum, E. Beche, A. Chambaudet, F. Jaffiol, Modifications of polypropylene surface properties by He^+ ion implantation, J. Polym. Sci. Part B: Polym. Phys. 41 (2003) 1183.
[11] A. Toth, V.S. Khotimsky, I. Bertoti, G. Marletta, Particle-beam treatment of organosilicon gas separation membranes: a novel way of controlling their mass transport properties, J. Appl. Polym. Sci. 60 (1996) 1883.
[12] A. Toth, T. Bell, I. Bertoti, M. Mohai, B. Zelei, Surface modification of polyethylene by low keV ion beams, Nucl. Instrum. Methods Phys. Res. Sect. B – Beam Interact. Mater. Atoms 148 (1999) 1131.
[13] G.Z. Liang, T.L. Lu, X.Y. Ma, H.X. Yan, Z.H. Gong, Synthesis and characteristics of radiation-grafted membranes for fuel cell electrolytes, Polym. Int. 52 (2003) 1300.
[14] H.E. Kausch, Radiation Effects on Polymers for Biological Use, Springer-Verlag, New York, 2003.
[15] M.L. Everett, G.B. Hoflund, Chemical alteration of poly(tetrafluoroethylene) teflon induced by exposure to vacuum ultraviolet radiation and comparison with exposure to hyperthermal atomic oxygen, J. Polym. Sci. Part A: Polym. Chem. 43 (2005) 552.
[16] G.B. Hoflund, M.L. Everett, Chemical alteration of poly(vinyl fluoride) tedlar by hyperthermal atomic oxygen, Appl. Surf. Sci. 239 (2005) 367.
[17] M. Bryjak, G. Pozniak, I. Gancarz, W. Tylus, Microwave plasma in preparation of new membranes, Desalination 163 (2004) 231.
[18] M. Bryjak, I. Gancarz, G. Pozniak, Plasma-modified porous membranes, Chem. Papers-Chem. Zvesti 54 (2000) 496.
[19] M. Bryjak, I. Gancarz, Plasma treatment of polyethylene ultrafiltration membranes, Angew. Makromol. Chem. 219 (1994) 117.
[20] S. Han, W.K. Choi, K.H. Yoon, S.K. Koh, Surface reaction on polyvinylidenefluoride (pvdf) irradiated by low energy ion beam in reactive gas environment, J. Appl. Polym. Sci. 72 (1999) 41.
[21] E. Wilusz, W. Zukas, Z.A. Fekete, F.E. Karasz, Ion beam modification of permselective membranes for chemical biological protective clothing, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 45 (2004) 7.
[22] Z.A. Fekete, E. Wilusz, F.E. Karasz, Modeling of displacement damage in an ion-beam-modified perfluorosulfonate ionomer, J. Polym. Sci. Part B: Polym. Phys. 42 (2004) 1343.
[23] M. Guenther, K. Sahre, G. Suchaneck, G. Gerlach, K.-J. Eichhorn, Influence of ion-beam induced chemical and structural modification in polymers on moisture uptake, Surf. Coat. Technol. 142–144 (2001) 482.
[24] K. Dworecki, M. Drabik, T. Hasegawa, S. Wasik, Modification of polymer membranes by ion implantation, Nucl. Instrum. Methods Phys. Res. Sect. B: Beam Interact. Mater. Atoms 225 (2004) 483.

[25] Z.S. Tong, M.Z. Wu, T.S. Pu, Z.Y. Zhang, J. Zhang, R.P. Jin, D.Z. Zhu, F.Y. Zhu, D.X. Cao, J.Q. Cao, The conductive behavior and structural characteristics in the I+-beam-implanted layer of plasma-polymerized pyrrole film, J. Appl. Polym. Sci. 69 (1998) 1743.
[26] J. Zhang, M.Z. Wu, T.S. Pu, Z.Y. Zhang, R.P. Jin, Z.S. Tong, D.Z. Zhu, D.X. Cao, F.Y. Zhu, J.Q. Cao, Investigation of the plasma polymer deposited from pyrrole, Thin Solid Films 307 (1997) 14.
[27] Z.S. Tong, M.Z. Wu, T.S. Pu, J. Zhang, Z.Y. Zhang, R.P. Jin, D.Z. Zhu, F.Y. Zhu, D.X. Cao, J.Q. Cao, The surface conduction induced by ar+ and the characteristics in this irradiated surface layer for plasma-polymerized pyrrole film, Appl. Surf. Sci. 119 (1997) 93.
[28] Z.S. Tong, T.S. Pu, M.Z. Wu, Z.Y. Zhang, J. Zhang, R.P. Jin, D.Z. Zhu, D.X. Cao, F.Y. Zhu, J.Q. Cao, The study of damaged layer induced by ar+ irradiation in plasma-polymerized thiophene film, Synth. Met. 79 (1996) 85.
[29] C. Moreau, R. Antony, A. Moliton, B. Francois, Sensitive thermoelectric power and conductivity measurements on implanted polyparaphenylene thin films, Adv. Mater. Opt. Electron. 7 (1997) 281.
[30] J. Davenas, V. Massardier, V.H. Tran, Conducting polymer synthesis via ion beam induced precursor conversion, Nucl. Instrum. Methods Phys. Res. Sect. B: Beam Interact. Mater. Atoms 112 (1996) 120.
[31] A.G. MacDiarmid, Synthetic metals: a novel role for organic polymers, Synth. Met. 125 (2001) 11.
[32] K. Gurunathan, A.V. Murugan, R. Marimuthu, U.P. Mulik, D.P. Amalnerkar, Electrochemically synthesised conducting polymeric materials for applications towards technology in electronics, optoelectronics and energy storage devices, Mater. Chem. Phys. 61 (1999) 173.
[33] A.J. Lovinger, L.J. Rothberg, Electrically active organic and polymeric materials for thin-film-transistor technologies, J. Mater. Res. 11 (1996) 1581.
[34] J. Pellegrino, The use of conducting polymers in membrane-based separations - a review and recent developments, Adv. Membr. Technol. 984 (2003) 289.
[35] D. Hohnholz, A.G. MacDiarmid, Line patterning of conducting polymers: new horizons for inexpensive, disposable electronic devices, Synth. Met. 121 (2001) 1327.
[36] M.R. Anderson, B.R. Mattes, H. Reiss, R.B. Kaner, Gas separation membranes—a novel application for conducting polymers, Synth. Met. 41 (1991) 1151.
[37] M.R. Anderson, B.R. Mattes, H. Reiss, R.B. Kaner, Conjugated polymer-films for gas separations, Science 252 (1991) 1412.
[38] H.G. Xue, Z.Q. Shen, Y.F. Li, Polyaniline-polyisoprene composite film based glucose biosensor with high permselectivity, Synth. Met. 124 (2001) 345.
[39] J. Davenas, X.L. Xu, Diffusion of iodine into polyimide films modified by ion-bombardment, Nucl. Instrum. Methods Phys. Res., Sect. B: Beam Interact. Mater. Atoms B 71 (1992) 33.
[40] X.L. Xu, M.R. Coleman, U. Myler, P.J. Simpson, Postsynthesis method for development of membranes using ion beam irradiation of polyimide thin films, ACS Symp. Ser. 744 (2000) 205.
[41] X.L. Xu, J.Y. Dolveck, G. Boiteux, M. Escoubes, M. Monchanin, J.P. Dupin, J. Davenas, Ion-beam irradiation effect on gas permeation properties of polyimide films, J. Appl. Polym. Sci. 55 (1995) 99.
[42] X.L. Xu, M.R. Coleman, U. Myler, P.J. Simpson, Ion beam irradiation-an efficient method to modify the subnanometer scale microstructure of polymers in a controlled way, Mater. Res. Soc. Symp. Proc. 540 (1999) 255.
[43] V. Svorcik, K. Proskova, V. Rybka, V. Hnatowicz, Water diffusion in polyethylene modified by ion irradiation, Polym. Degrad. Stab. 60 (1998) 431.
[44] E. Wilusz, Q. Truong, W.X. Zukas, D.H. McCullough, J. Li, S.L. Regen, Z.A. Fekete, F.E. Karasz, Membrane Development for the Next Generation of Chemical Biological Clothing, CBIP Conference, Charleston SC, 2006, proceedings available at http://www.dtic.mil/ndia/2006cbip/wilusz.pdf.
[45] M. Escoubes, J.Y. Dolveck, J. Davenas, X.L. Xu, G. Boiteux, Ion beam modification of polyimide membranes for gas permeation, Nucl. Instrum. Methods Phys. Res., Sect. B: Beam Interact. Mater. Atoms 105 (1995) 130.
[46] E. Wilusz, W.X. Zukas, Z.A. Fekete, F.E. Karasz, Ion beam modification of permselective membranes for chemical biological protective clothing, Polym. Prep. ACS 45 (2004) 7.
[47] Z.A. Fekete, E. Wilusz, F.E. Karasz, Integrally skinned membrane preparation by medium energy ion beam modification of the perfluorosulfonate ionomer Nafion, Polym. Prep. ACS 42 (2002) 213.
[48] E.H. Lee, M.B. Lewis, P.J. Blau, L.K. Mansur, Improved surface-properties of polymer materials by multiple ion-beam treatment, J. Mater. Res. 6 (1991) 610.
[49] V. Hnatowicz, V. Havranek, J. Kvitek, V. Perina, V. Svorcik, V. Rybka, Modifications of polypropylene induced by the implantation of iodine ions, Jpn. J. Appl. Phys., Part I: Regular Papers and Short Notes 32 (1993) 1810.
[50] V. Hnatowicz, J. Kvitek, V. Svorcik, V. Rybka, Oxygen incorporation in polyethylene and polypropylene implanted with F+, as+ and I+ ions at high-dose, Appl. Phys. A: Solids Surf. 58 (1994) 349.
[51] J.F. Ziegler, J.P. Biersack, U. Littmark, The Stopping and Range of Ions in Solids, Pergamon Press, New York, 1985.
[52] J.F. Ziegler, Srim-2003, Nucl. Instrum. Methods Phys. Res. Sect. B: Beam Interact. Mater. Atoms 219–20 (2004) 1027.
[53] J.F. Ziegler, J.M. Manoyan, The stopping of ions in compounds, Nucl. Instrum. Methods Phys. Res. Sect. B: Beam Interact. Mater. Atoms B35 (1988) 215.
[54] A. Toth, I. Bertoti, E. Szilagyi, H. Dong, T. Bell, A. Juhasz, P.M. Nagy, Surface characterization of ultrahigh molecular weight polyethylene after nitrogen ion implantation, Surf. Interface Anal. 30 (2000) 434.
[55] Z.A. Fekete, Srim-scripts: scripts for driving and evaluating ion implantation simulations by Ziegler's Srim/Trim Software, 2005, Available via http://www.staff.u-szeged.hu/~fekete/srim_trim-scripts/.
[56] E.A. Hoffmann, Z.A. Fekete, L.S. Korugic-Karasz, F.E. Karasz, E. Wilusz, Theoretical and experimental X-ray photoelectron spectroscopy investigation of ion-implanted Nafion, J. Polym. Sci. Part A-Polym. Chem. 42 (2004) 551.
[57] K.E. Aasmundtveit, E.J. Samuelsen, K. Hoffmann, E. Bakken, P.H.J. Carlsen, Structural studies of polyalkylthiophenes with alternating sidechain positioning, Synth. Met. 113 (2000) 7.
[58] A.F. Burenkov, F.F. Komarov, M.A. Kumakhov, M.M. Temkin, Tables of Ion Implantation Spatial Distributions, Gordon and Breach, New York, 1986.
[59] E. Bode, C. Hoempler, Transport resistances during pervaporation through a composite membrane: experiments and model calculations, J. Membr. Sci. 113 (1996) 43.
[60] L.M. Robeson, W.F. Burgoyne, M. Langsam, A.C. Savoca, C.F. Tien, High-performance polymers for membrane separation, Polymer 35 (1994) 4970.
[61] W.J. Koros, G.K. Fleming, Membrane-based gas separation, J. Membr. Sci. 83 (1993) 1.